Superfluid $^4$He

Phase diagram:
- Solid
- Normal liquid
- Superfluid
- Liquid-gas critical point
- Liquid-gas transition
- Gas

$T_a = 2.18^\circ K$

Liquid-gas transition is 1st order - there is a latent heat.
Normal-superfluid transition is 2nd order - no latent heat.

Specific heat:

$\frac{C_v}{N k_B}$

Diverges at $T_c$ where "A" line is crossed.

1. Shape of $C_v$ reminds one of the curve in $C_v$ for Bose-Einstein condensation in ideal boson gas, although here $C_v$ diverges at $T_c$.

2. In superfluid phase, some fraction $\phi_s(r)/\phi$

$[\phi_s = \text{superfluid density}; \phi = \text{total density}]$ of the fluid flows without any dissipation and carries no entropy - reminds one of the condensate of Bose-Einstein condensation.
for $^4$He mass $m = 6.65 \times 10^{-24}$ g, and $^4$He fluid specific volume $V = 27.60$ cm$^3$/mole, one finds a Bose-Einstein condensation temperature of $T_c = 3.13$ K, not far from $T_a = 2.18$ K.

These observations suggested that superfluidity in $^4$He was related to Bose-Einstein condensation (BEC) of an ideal gas.

However

1. BEC transition line in P-T plane, $P_c \propto T^{5/2}$, has a positive slope, whereas $T$-line of $^4$He has a negative slope.

2. As demonstrated by Landau, the condensate of BEC in an ideal Bose gas is not a superfluid.

Landau's argument

Consider a condensate (all particles in same state) of total mass $M$, flowing with velocity $\vec{V}$ down a pipe. It has total momentum $\vec{P} = MV$. In the rest frame of this fluid, consider an excitation that is created with momentum $\vec{p}$ and energy $E(\vec{p})$. 
Back in the rest frame of the pipe, the change in energy due to the creation of the excitation is (in the limit of large total mass $M \to \infty$)

$$\Delta E = \frac{(\vec{P} + \vec{p})^2}{2M} + \epsilon(\vec{p}) - \frac{P^2}{2M}$$

$$= \frac{\vec{P} \cdot \vec{P}}{2M} + \frac{P^2}{2M} + \epsilon(\vec{p})$$

$$\Delta E = \epsilon(\vec{p}) + \vec{p} \cdot \vec{v}$$  since $\frac{\vec{P}}{M} = \vec{v}$, and

$$\frac{P^2}{2M} \to 0$$ for large $M$

If $\Delta E < 0$, then it will be energetically favorable to create such excitations of momentum $\vec{p}$ - the motion of the fluid will therefore excite particles out of the condensate and degrade the flow, i.e. the system will not display superfluidity.

$$\Delta E < 0 \Rightarrow \epsilon(\vec{p}) < -\frac{\vec{p} \cdot \vec{v}}{\vec{P}}$$

For $\vec{p} \parallel -\vec{v}$, $\Rightarrow \epsilon(\vec{p}) < \frac{v}{\vec{P}}$

For an ideal Bose gas, $\epsilon(p) = \frac{p^2}{2m}$, so

$$\frac{\epsilon(\vec{p})}{\vec{p}} = \frac{\vec{p}}{2m}$$ will always be less than flow velocity $v$, for sufficiently small $p$. 

So the condensate of an ideal Bose gas, flowing with any velocity \( v \) no matter how small, will always excite particles out of the condensate into low-lying excited states, and hence will not be a superfluid.

However, from experiments such as neutron scattering and specific heat, it was known that the low-lying excitation spectrum of \(^4\)He was not free particle-like, but rather as shown below:

\[
\frac{E(p)}{k_B} = \begin{cases}
20k & \text{at small } p, \\
10k & \text{at higher } p \text{ there is a dip.}
\end{cases}
\]

Excitations in the slow \( p \)
linear region are phonons, or sound waves. Excitations near the dip were called "rotons."

\[
\frac{\Delta}{k_B} = 8.7^\circ K
\]

\[
C = 2.4 \times 10^4 \text{ cm/s}
\]

\[
m^* \approx 0.16 m_e
\]

\[
p_0 \approx 1.9 \text{ Å}^{-1}
\]
As the fluid flow velocity \( v \) is increased from zero, the condition \( \frac{\varepsilon(p)}{p} = v \) will first be reached at the velocity \( v^* \) shown below.

\[ v^* = 60 \text{ m/s} \]

for \( v < v^* \), \( \frac{\varepsilon(p)}{p} > v \) for all values of \( p \), and so no particles will be excited out of the condensate by the flow. The fluid is now a superfluid!

Experimentally, while superfluidity does exist in \(^4\text{He}\) at low flow velocities, the critical velocity \( v_{\text{crit}} \), above which the flow becomes dissipative, is much lower than the \( v^* \) above, and is strongly dependent on the size and shape of the container. This is due to the onset of turbulence accompanied by the proliferation of quantized vortices in the condensate flow.
The fact that the spectrum $E(p)$ is linear at small $p$, and not free particle-like, is due to the fact that the $^4$He atoms are not an ideal gas — in fact, the $^4$He atoms are strongly interacting. This should not be surprising — the $^4$He is a liquid and not a gas, particles collide with other quasiparticles to sound modes as the low-energy excitations, rather than free “ballistic” motion of individual atoms.

One can show that for an interacting Bose gas, even for weak interactions, the small-$p$ part of the excitation spectrum always is phonon-like, i.e. linear (see Pathria §10.3 or Sakurai Phys 509!). Superfluidity can only exist for interacting Bose systems.

Because interactions between $^4$He atoms are not weak, there is no good microscopic theory of superfluidity in $^4$He. Calculations can, however, be performed for weak interactions. This has led people to look for superfluidity or BEC in weakly interacting Bose gases. The search was finally successful with the observation of BEC in magnetically trapped, laser cooled, dilute atomic gases (producing two Nobel prizes!).
Bose-Einstein Condensation in laser cooled gases

Gases of alkali atoms \textit{Li}, \textit{Na}, \textit{K}, \textit{Rb}, \textit{Cs}

- all have a single 5-electron in outermost shell, important for trapping of laser cooling
- use isotopes such that total intrinsic spin of all electrons and nucleons add up to an integer \( n \)

\( \implies \) atoms are bosons

- all have a net magnetic moment - used to confine dilute gas of atoms in a "magnetic trap"
- use "laser cooling" to get very low temperatures in low density gases, to try and see \( \text{BEC} \)

magnetic trap \( \rightarrow \) effective harmonic potential for atoms

\[ V(r) = \frac{1}{2} m \omega_0^2 r^2 \quad \omega_0 \approx 2 \pi \times 100 \text{ Hz} \]

1995 - \( 1 \times 10^3 \) atoms with \( T_c \approx 100 \text{ nK} \)

1999 - \( 1 \times 10^8 \) atoms with \( T_c \approx 1 \text{ nK} \) gas size \( \approx \) many microns

How was \( \text{BEC} \) in these systems observed?

Energy levels of ideal (non-interacting)

bosons in harmonic trap

\[ E(n_x, n_y, n_z) = (n_x + n_y + n_z + \frac{3}{2}) \hbar \omega_0 \]

\( n_x, n_y, n_z \) integers

Ground state condensate wavefunction

\[ \psi_0(r) \sim e^{-r^2/2a^2} \text{ with } a = \left( \frac{\hbar}{m \omega_0} \right)^{1/2} \]

\( a \approx 1 \text{ mm} \) for current traps
$\Rightarrow$ Condensate has spatial extent $\sim a$

The spatial extent of the $n^{th}$ excited energy level is roughly

$$m_0 w_0^2 \langle r^2 \rangle \sim E(n) \approx n \hbar w_0$$

$$\Rightarrow \langle r^2 \rangle \sim \frac{n \hbar}{m_0 w_0} \quad \text{or} \quad \sqrt{\langle r^2 \rangle} = \left(\frac{n \hbar}{m_0 w_0}\right)^{\frac{1}{2}}$$

For $k_B T \gg \hbar w_0$, the atoms are excited up to level $n \sim \frac{k_B T}{\hbar w_0}$

$\Rightarrow$ spatial extent of the normal component of the gas is

$$R \sim \left(\frac{n \hbar}{m_0 w_0}\right)^{\frac{1}{2}} \sim \left(\frac{\hbar k_B T}{\hbar m w_0^2}\right)^{\frac{1}{2}} = \left(\frac{k_B T}{m w_0}\right)^{\frac{1}{2}}$$

$$R \sim a \left(\frac{k_B T}{\hbar w_0}\right)^{\frac{1}{2}} \Rightarrow a$$

If $T_c$ is the BEC transition temperature, then for $T > T_c$ one sees a more or less uniform cloud of atoms with radius $R \sim a \left(\frac{k_B T}{\hbar w_0}\right)^{\frac{1}{2}} \gg a$. But when one cools to $T < T_c$, one now has a finite fraction of the atoms condensed in the ground state, superimposed on the atomic cloud of radius $R$ one sees the growth of a sharp peak in density at the center of cloud - this peak has a radius $a \ll R$. 
To find $T_c$, \((\text{use } z = 1 \text{ at } T \leq T_c)\)

\[
m = m_0 + \int_0^\infty \int_0^\infty \int_0^\infty \frac{1}{e^{(n_x + n_y + n_z) \hbar \omega_0 / k_B T} - 1} \, \text{d}x \, \text{d}y \, \text{d}z
\]

\[
= m_0 + \left(\frac{k_B T}{\hbar \omega_0}\right)^3 \int_0^\infty \int_0^\infty \int_0^\infty \frac{1}{e^{(x+y+z) \hbar \omega_0 / k_B T} - 1} \, \text{d}x \, \text{d}y \, \text{d}z
\]

\[
= m_0 + \left(\frac{k_B T}{\hbar \omega_0}\right)^3 k^3
\]

at $T_c$, $m_0 = 0 \Rightarrow k_B T_c = \hbar \omega_0 \left(\frac{m}{\xi(3)}\right)^{1/3}$

condensate density $m_0(T) = m(1 - \left(\frac{T}{T_c}\right)^3)^{1/3}$

different from ideal free gas due to presence of magnetic trapping potential
Classical ideal gas with internal degrees of freedom

Assume \( m \frac{a^3}{k} \ll 1 \) so molecules are classical
as far as their translational motion is concerned
\[
\Rightarrow \Omega_N = \left( \frac{1}{N!} \right) \sum q_1 J_N
\]

\( \Omega_1 \) is single molecule partition function

Suppose molecule has internal degrees of freedom, so that its energy is
\[
\frac{p_i^2}{2m} + \epsilon_i
\]
where \( \epsilon_i \) are the internal energy levels

Then
\[
\Omega_1 = \int \frac{d^3 \mathbf{r}}{h^3} \int \frac{d^3 \mathbf{p}}{h^3} \sum_i e^{-\beta \epsilon_i} = \frac{V}{\beta^3} \sum_i e^{-\beta \epsilon_i}
\]

\( \beta = \left( \frac{\hbar^2}{2\pi m k_B T} \right)^{1/2} \)

Sun over all internal states of molecule

Let
\[
q = \sum_i e^{-\beta \epsilon_i}
\]

then
\[
\Omega_1 = \frac{V}{\beta^3} q
\]

\[
\Omega_N = \frac{1}{N!} \left[ \frac{V}{\beta^3} q \right]^N = \Omega_N q^N
\]

\( \Omega_N^{(0)} = \frac{1}{N!} \left[ \frac{V}{\beta^3} \right]^N \)

\( \Omega_N^{(0)} \) partition function for point particle
Helmholtz free energy

\[ A(T, V, N) = -k_B T \ln (Q_N) \]

\[ = -k_B T \ln (Q_N^{(0)}) - k_B T \ln q \]

\[ = A^{(o)} - k_B T \ln q \quad \uparrow \quad \text{free energy of internal degree of freedom} \]

\[ \quad \text{free energy for point particles} \]

effect of internal degrees of freedom are additive to free energy

\[ A = A^{(o)} + A^{\text{int}} \quad A^{\text{int}} = -k_B T N \ln q \]

Note: \( q \) has no dependence on \( N \) or \( V \), only depends on \( T \).

\[ \Rightarrow \text{pressure} \quad p = -\frac{\partial A}{\partial V} = \frac{\partial A^{(o)}}{\partial V} \quad \text{unaffected by internal degree of freedom} \]

chemical potential

\[ \mu = +\frac{\partial A}{\partial N} = \frac{\partial A^{(o)}}{\partial N} - k_B T \ln q \]

\[ = \mu^{(o)} + \mu^{\text{int}} \quad \mu^{\text{int}} = -k_B T \ln q \quad \text{intenal degrees of freedom add } T\text{-dependent constant to } \mu \]

entropy

\[ S = -\frac{\partial A}{\partial T} = -\frac{\partial A^{(o)}}{\partial T} + \frac{2}{\partial T} (k_B T \ln q) \]

\[ S = S^{(o)} + N k_B \ln q + N k_B T \frac{2}{\partial T} \ln q \]

\[ S = S^{(o)} + S^{\text{int}} \]
Energy: \[ A = E - TS \]
\[ \Rightarrow E = A + TS \]
\[ = E^{(0)} + A_{\text{int}} + T S_{\text{int}} \]
\[ = E^{(0)} + \varepsilon_{\text{int}} \]

\[ E_{\text{int}} = -k_b T N \ln g + T N k_b \ln g + N k_b T^2 \frac{\partial \ln g}{\partial T} \]
\[ = N k_b T^2 \frac{\partial \ln g}{\partial T} \]

Specific heat:
\[ C_V = \left( \frac{\partial E}{\partial T} \right)_{V,N} = C_V^{(0)} + C_{V\text{int}} \]

\[ C_{V\text{int}} = \frac{\partial}{\partial T} \left( N k_b T^2 \frac{\partial \ln g}{\partial T} \right) \]
\[ = 2 N k_b T \frac{\partial \ln g}{\partial T} + N k_b T^2 \frac{\partial^2 \ln g}{\partial T^2} \]

The internal degrees of freedom can often be separated into different physical sources:
1) electronic excitation
2) vibrational excitation of bonds
3) rotational motion of molecule

In many cases these different modes of excitation are only weakly interacting, so one can write:

\[ E_i = E_{\text{elec}} + E_{\text{ vib}} + E_{\text{ rot}} \]

\[ \beta = \sum_i e^{-\beta (E_{\text{elec}} + E_{\text{ vib}} + E_{\text{ rot}})} = \left( \sum_i e^{-\beta E_{\text{elec}}} \right) \left( \sum_i e^{-\beta E_{\text{ vib}}} \right) \times \left( \sum_i e^{-\beta E_{\text{ rot}}} \right) \]
where \( \epsilon_e, \ \epsilon_v, \ \epsilon_r \) stand for the quantum numbers associated with the electronic, vibrational, and rotational degrees of freedom.

\[
\mathcal{F} = \mathcal{F}_{\text{elec}} + \mathcal{F}_{\text{vib}} + \mathcal{F}_{\text{rot}}
\]

\[
\mathcal{A}_{\text{tot}} = \mathcal{A}_{\text{elec}} + \mathcal{A}_{\text{vib}} + \mathcal{A}_{\text{rot}}
\]

**Example**

A monoatomic gas - particles are single atoms. Internal degrees of freedom are excitations to higher electron levels. Electronic excitation energies are \( \sim 1 \text{eV} \sim 0(10^4 \text{K}) \) so at room temperatures, only the lowest excited states can be populated.

\[
\mathcal{F} = \mathcal{F}_0 e^{-\beta \epsilon_0} + \mathcal{F}_1 e^{-\beta \epsilon_1}
\]

where \( \epsilon_0 \) and \( \epsilon_1 \) are energies of ground + 1st excited states; \( \mathcal{F}_0 \) and \( \mathcal{F}_1 \) are their degeneracies.

\[
\mathcal{F} = \mathcal{F}_0 e^{-\beta \epsilon_0} \left(1 + \frac{\mathcal{F}_1}{\mathcal{F}_0} e^{-\beta \Delta \epsilon}\right) \quad \Delta \epsilon = \epsilon_1 - \epsilon_0
\]

\[
\mathcal{A}_{\text{tot}} = -k_b T N \ln \left(1 + \frac{\mathcal{F}_1}{\mathcal{F}_0} e^{-\beta \Delta \epsilon}\right) + N \epsilon_0 - k_b T N \ln g
\]
\[ C_{v, \text{mit}} = \frac{2}{\partial T} \left( N k_b T^2 \frac{2}{\partial T} \ln g \right) \]
\[ = \frac{2}{\partial T} \left( N k_b T^2 \frac{2}{\partial T} \left( -\ln g_0 + \frac{g_1}{k_b T} \ln \left( 1 + g_1 \frac{e^{-\beta \Delta \varepsilon}}{g_0} \right) \right) \right) \]
\[ = \frac{2}{\partial T} \left( N k_b T^2 \left[ \frac{g_0}{k_b T^2} + \frac{g_1}{g_0} \frac{e^{-\beta \Delta \varepsilon}}{1 + g_1 \frac{e^{-\beta \Delta \varepsilon}}{g_0}} \right] \right) \]
\[ = N \frac{2}{\partial T} \left[ \frac{g_0}{k_b T^2} + \frac{\Delta \varepsilon (g_1 g_0) e^{-\beta \Delta \varepsilon}}{1 + g_1 \frac{e^{-\beta \Delta \varepsilon}}{g_0}} \right] \]
\[ = N \Delta \varepsilon (g_1 g_0) \frac{\left[ 1 + g_1 \frac{e^{-\beta \Delta \varepsilon}}{g_0} e^{-\beta \Delta \varepsilon} \left( \frac{\Delta \varepsilon}{k_b T^2} \right) - e^{-\beta \Delta \varepsilon} \right]}{\left[ 1 + g_1 \frac{e^{-\beta \Delta \varepsilon}}{g_0} \right]^2} \]
\[ = N \Delta \varepsilon \frac{g_1}{g_0} e^{-\beta \Delta \varepsilon} \frac{\Delta \varepsilon}{k_b T^2} \]

\[ C_{v, \text{mit}} = N k_b \left( \frac{\Delta \varepsilon}{k_b T} \right)^2 \left( \frac{g_1}{g_0} \right) e^{-\beta \Delta \varepsilon} \frac{\Delta \varepsilon}{k_b T} \left[ 1 + \frac{g_1}{g_0} e^{-\beta \Delta \varepsilon} \right]^2 \]

"Schottky anomaly" typical of excitation of one energy level
Vibrational excitations

\[ E_{\text{vib}} = (n + \frac{1}{2}) \hbar \omega_0 \]

\( \omega_0 \) is vibrational frequency related to stiffness of bond + mass of atoms. \( \omega_0 = \sqrt{\frac{k}{m}} \)

\[ q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta (n+\frac{1}{2}) \hbar \omega_0} = e^{-\beta \hbar \omega_0 / 2} \sum_{n=0}^{\infty} \left( e^{-\beta \hbar \omega_0} \right)^n \]

\[ q_{\text{vib}} = e^{-\beta \hbar \omega_0 / 2} \cdot \frac{1}{1 - e^{-\beta \hbar \omega_0}} = \frac{1}{2 \sinh (\beta \hbar \omega_0 / 2)} \]

\[ C_{\text{vib}} = \frac{2}{aT} \left( Nk_bT \frac{2}{aT} \ln q_{\text{vib}} \right) \]

\[ = \frac{2}{aT} \left( Nk_bT^2 \frac{2}{aT} \left[ -\ln \left( e^{\frac{\beta \hbar \omega_0}{2}} - e^{-\beta \hbar \omega_0 / 2} \right) \right] \right) \]

\[ = \frac{2}{aT} \left( Nk_bT^2 \left( -1 \right) \frac{(-\frac{\hbar \omega_0}{2k_BT^2}) e^{\frac{\beta \hbar \omega_0}{2}} - \left( \frac{\hbar \omega_0}{2k_BT^2} \right) e^{-\frac{\beta \hbar \omega_0}{2}}}{e^{\frac{\beta \hbar \omega_0}{2}} - e^{-\frac{\beta \hbar \omega_0}{2}}} \right) \]

\[ = \frac{2}{aT} \left( Nk_bT^2 \frac{\hbar \omega_0}{2k_BT^2} \frac{e^{\frac{\beta \hbar \omega_0}{2}} + e^{-\frac{\beta \hbar \omega_0}{2}}}{e^{\frac{\beta \hbar \omega_0}{2}} - e^{-\frac{\beta \hbar \omega_0}{2}}} \right) \]

\[ = \frac{N \hbar \omega_0}{2} \frac{2}{aT} \left( \coth \left( \frac{\beta \hbar \omega_0}{2} \right) \right) \]
\[ C_{v,\text{vib}} = N k_B \left( \frac{\hbar \omega_0}{k_B T} \right)^2 \frac{1}{4} \frac{1}{\text{sinh}^2 \left( \frac{\beta \hbar \omega_0}{2} \right)} \]

\[ = N k_B \left( \frac{\hbar \omega_0}{k_B T} \right)^2 \frac{1}{4} \frac{1}{\text{sinh}^2 \left( \frac{\beta \hbar \omega_0}{2} \right)} \]

\[ C_{v,\text{vib}} = N k_B \left( \frac{\hbar \omega_0}{k_B T} \right)^2 \frac{1}{4} \frac{1}{\left[ e^{\beta \hbar \omega_0} - 1 \right]^2} \]

For large \( \beta \hbar \omega_0 = \frac{\hbar \omega_0}{k_B T} \ll 1 \) or high temp

\[ C_{v,\text{vib}} \approx N k_B \left( \frac{\hbar \omega_0}{k_B T} \right)^2 \frac{1}{4} \frac{1}{\left( \frac{\hbar \omega_0}{k_B T} \right)^2} = N k_B \]

**classical equipartition result**

At low \( T \), \( \beta \hbar \omega_0 \gg 1 \)

\[ C_{v,\text{vib}} = N k_B \left( \frac{\hbar \omega_0}{k_B T} \right)^2 e^{-\frac{\hbar \omega_0}{k_B T}} \]

\[ C_{v,\text{vib}} \]

\[ 0 \quad \frac{\hbar \omega_0}{k_B} \quad T \]

\[ N k_B \]
for a polyatomic molecule with many bonds
of freq \( \omega_1 > \omega_2 > \omega_3 \), \( C_{v, \text{vib}} \) is just sum of terms
for each bond

\[
\begin{align*}
C_{v, \text{vib}} & = 3Nk_B \\
& = 2Nk_B \\
& = Nk_B \\
& = k_B T
\end{align*}
\]

**Rotational degree of freedom**

\[
E_{\text{rot}} = \frac{l(l+1)\hbar^2}{2I}
\]

\[
\begin{align*}
\mathcal{G}_{\text{rot}} & = \sum_{l=0}^{\infty} \left( 2l+1 \right) e^{-\beta \frac{l(l+1)}{2I}} \\
& \approx \frac{1}{\beta \frac{\hbar^2}{2I}} \quad \text{good when} \\
& \beta \frac{\hbar^2}{2I} \ll 1 \quad \text{at low temperatures}
\end{align*}
\]

\[
\begin{align*}
\text{deg. of angular momentum} & = \ell \\
\text{equiv. to} & = \ell
\end{align*}
\]

\[
\begin{align*}
\int_0^\infty (2l+1) e^{-\beta \frac{l(l+1)}{2I}} dl & = \frac{\beta \frac{\hbar^2}{2I}}{\ell (\ell + 1)} \\
\int_0^\infty (2l+1) e^{-\beta \frac{\hbar^2}{2I}} dl & \approx \frac{1}{\beta \frac{\hbar^2}{2I}} \quad \text{good when} \\
& \beta \frac{\hbar^2}{2I} \ll 1 \quad \text{at low temperatures}
\end{align*}
\]
\[ \Theta_{\text{rot}} = \int_0^{\infty} dx \ e^{-\beta \frac{x^2}{2 \hbar^2}} = \frac{2 \pi}{\beta \hbar^2} = \frac{2 \pi k_B T}{\hbar^2} = \frac{T}{\Theta_K} \]

where \( \Theta_K = \frac{\hbar^2}{2 \pi k_B} \)

\[ C v n T = \frac{\partial}{\partial T} \left( N k_B T^2 \frac{\partial}{\partial T} \ln \Theta_{\text{rot}} \right) \]

\[ = \frac{\partial}{\partial T} \left( N k_B T^2 \frac{\partial}{\partial T} \ln \left( \frac{T}{\Theta_K} \right) \right) \]

\[ = \frac{\partial}{\partial T} \left( N k_B T^2 \frac{1}{T} \right) = N k_B \text{ classical equipartition result.} \]

To do better than approx sum by integral use

Euler–Maclaurin series

\[ \sum_{n=0}^{\infty} f(n) = \int_0^\infty f(x) \, dx + \frac{1}{2} f(0) - \frac{1}{12} f'(0) + \frac{1}{720} f^{(5)}(0) + \ldots \]

using \( f(x) = (2x+1) \exp\left(-x(x+1) \frac{\Theta_K}{T}\right) \)

\[ \Rightarrow \Theta_{\text{rot}} = \frac{T}{\Theta_K} + \frac{1}{3} + \frac{1}{15} \frac{\Theta_K}{T} + \frac{4}{315} \left( \frac{\Theta_K}{T} \right)^2 + \ldots \]

\[ C v n T = N k_B \left\{ 1 + \frac{1}{45} \left( \frac{\Theta_K}{T} \right)^2 + \frac{16}{945} \left( \frac{\Theta_K}{T} \right)^3 + \ldots \right\} \]

For low \( T \), therefore \( \frac{\Theta_K}{T} >> k_B T \) or \( \Theta_K >> T \)

the first few terms of the series

\[ \Theta_{\text{rot}} = 1 + 3 e^{-2 \Theta_K/T} + 5 e^{-6 \Theta_K/T} + \ldots \]
$$C_{V, mnt} = 12 N k_B \left( \frac{\theta_R}{T} \right)^2 e^{-2\theta_R/T}$$